



Polymer Brushes

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Lecture: 5/7

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Outline

What you might know from before: Polymers are entropic springs where the end-to-end distance probability follows a Gaussian distribution.

Now we will extend this model to take two more things into account:

- The self-avoidance effect (excluded volume).
- The influence from a solvent around the polymer.

Then we look at polymer *brushes*, i.e. polymers with one end attached to a surface.



Repetition: Conformational Entropy

From the *freely jointed chain model*, the entropy as function of end-to-end distance is given by:

$$S(r) = \text{constant} - \frac{3k_B r^2}{2abN}$$

The expected value R for end-to-end distance is given from the “random walk” behavior:

$$\langle |r| \rangle = R = [abN]^{1/2}$$

Thus, to predict R we need:

- Monomer size a .
 - Number of monomers N .
 - Kuhn-length b (twice the *persistence length*).
- } or contour length



Repetition: Polymers as Entropic Springs

When the entropy is known as a function of chain elongation, we can get the free energy as a function of r for the random walk model:

$$G(r) = -TS(r) = \frac{3k_B T r^2}{2abN} + \text{constant}$$

The force required to stretch the chain is:

$$F(r) = \frac{\partial G}{\partial r} = \frac{3k_B T r}{abN}$$

The “spring constant” is:

$$\frac{\partial^2 G}{\partial r^2} = \frac{\partial F}{\partial r} = \frac{3k_B T}{abN}$$



Wikipedia: Spring

Note that it is easier to pull long and stiff polymers (counterintuitive).

Here all is based on conformational entropy, no interaction energies accounted for!



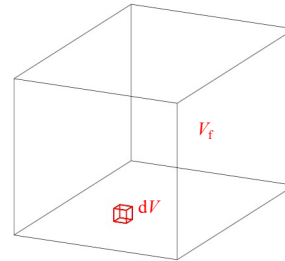
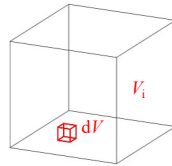
Repetition: Volumes and Entropy

Consider volume expansion from the viewpoint of statistical mechanics.

We can discretize the space available into a certain number of positions, each with volume dV , where a particle can be located. The entropy change is then:

$$\Delta S = k_B \log(W_f) - k_B \log(W_i) = k_B \log\left(\frac{W_f}{W_i}\right) = k_B \log\left(\frac{\frac{V_f}{dV}}{\frac{V_i}{dV}}\right) = k_B \log\left(\frac{V_f}{V_i}\right)$$

Now imagine the particle is a monomer...



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Self Avoiding Chains

Assume we have our N chain segments, each with volume v , in a total volume V . The *excluded volume* occupied by the coil is Nv .

We can now do a *mean field approximation*: We assume that the segment density is homogenous throughout the volume that the coil occupies.

The entropy loss per segment is then:

$$\Delta S_{\text{seg}} = k_B \log\left(\frac{V_f}{V_i}\right) = k_B \log\left(\frac{V - Nv}{V}\right) = k_B \log\left(1 - \frac{Nv}{V}\right) \approx -\frac{k_B Nv}{V} \quad \text{for small polymer volume fractions } (Nv/V)$$

We thus treat the polymer as a “gas” of monomers. Remember that the molecule is assumed to be long and flexible and it wobbles around (so the assumption is not crazy).

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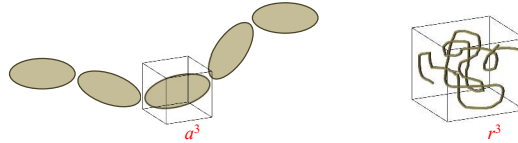
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Excluded Volume Entropy

We can assume that $V \approx r^3$ and probably $v \approx a^3$ but we just call it v for now:

$$\Delta S_{\text{seg}} = -\frac{k_B N v}{r^3}$$



We get the total free energy increase for the polymer due to the presence of itself by multiplying with N (all monomers) and temperature:

$$\Delta G_{\text{vol}}(r) = -NT\Delta S_{\text{seg}} = \frac{k_B T v N^2}{r^3}$$

The chain will want to expand to make ΔG_{vol} smaller but we must not forget the conformational entropy cost of stretching the chain:

$$G(r) = \frac{3k_B T r^2}{2abN} + \frac{k_B T v N^2}{r^3} + \text{constant}$$



Sanity Check: Osmotic Pressure?

Osmotic pressure Π with a second virial coefficient B is given by:

$$\Pi = k_B T [C + BC^2] \quad \text{"ideal" (dilute) behavior for } B = 0$$

Here C is concentration (inverse volume), which inside the coil is N/V :

$$\Pi = k_B T \left[\frac{N}{V} + B \left[\frac{N}{V} \right]^2 \right] \quad G = \Pi V = k_B T \left[N + \frac{BN^2}{V} \right]$$

The free energy increase due to the deviation from ideal behavior is:

$$\Delta G = \Pi V = k_B T \left[N + B \frac{N^2}{V} \right] - k_B T N = \frac{k_B T B N^2}{V}$$

Again assuming $V = r^3$, we see that $B = v$ so the osmotic pressure effect is equivalent.

We will look at energetic interactions soon...



Example of the Excluded Volume Effect

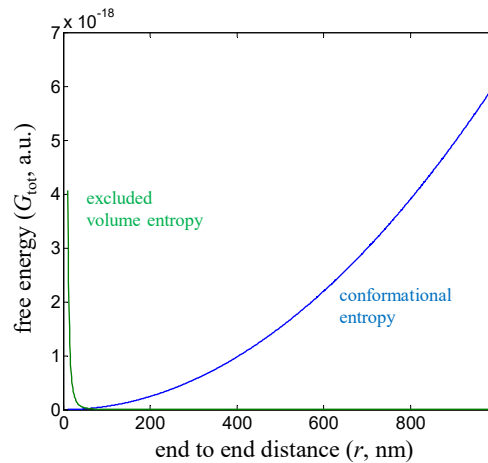
As an example we can plot the free energies as a function of r for:

$$\begin{aligned} N &= 1000 \\ a &= 1 \text{ nm} \\ b &= 1 \text{ nm} \\ v &= 1 \text{ nm}^3 \end{aligned}$$

For small r the excluded volume effect dominates entirely, but disappears very fast with (r^{-3}).

The conformational entropy loss increases steadily (r^2).

Minimum for some value of r !



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The Flory Radius

We can minimize G_{tot} with respect to r by taking the derivative:

$$\frac{\partial G_{\text{tot}}}{\partial r} = \frac{3k_{\text{B}}Tr}{abN} - \frac{3k_{\text{B}}TvN^2}{r^4}$$

Setting the derivative to zero will give the free energy minimum and thus the expected value of r (in other words R) from:

$$\frac{3k_{\text{B}}TR}{abN} = \frac{3k_{\text{B}}TvN^2}{R^4}$$

This gives us:

$$R^5 = abvN^3$$

So we arrive at an exponent of $3/5$ instead of $1/2$. We can denote this as the Flory radius:

$$R_{\text{F}} = [abv]^{1/5} N^{3/5}$$

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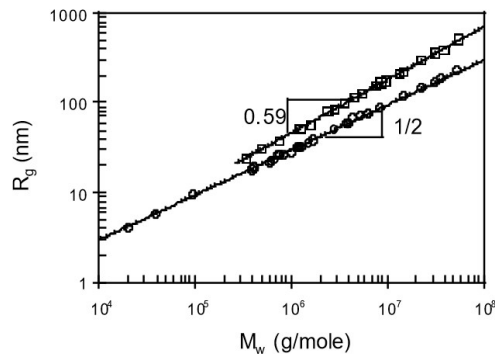
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Validity?

The “accurate” value of the exponent, based on the math of self-avoiding random walks, is 0.588... But experiments cannot discriminate this value from 3/5 (though from 1/2).



“radius of gyration” of polystyrene chains in a “theta-solvent” (cyclohexane at 34.5°C) and in a good solvent (benzene at 25°C)

Fetters et al.
Journal of Physical and Chemical Reference Data 1994, 23 (4), 619-640.



Who Cares About 1/2 or 3/5?

The value of the exponent is very important because N is a large number!

$$\frac{R_F}{R} = \frac{[abv]^{1/5} N^{3/5}}{[abN]^{1/2}} \approx N^{1/10}$$

Equal to 1.58 for $N = 100$ and 2.00 for $N = 1000$.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 17, NUMBER 3 MARCH, 1949

The Configuration of Real Polymer Chains*

PAUL J. FLORY
Department of Chemistry, Cornell University, Ithaca, New York
(Received August 23, 1948)

The average configuration of polymer molecules in solution is markedly influenced by the obvious requirement, ordinarily disregarded in problems relating to molecular configuration, that two elements of the molecule are forbidden from occupying the same location in space. The influence of spatial “interferences” between different segments of the molecule on its average configuration has been investigated by statistical and thermodynamic methods.

It is shown that if the average linear dimension of a polymer chain is to be taken proportional to a power of the chain length, that power must be greater than the value 0.50 previously deduced in the conventional “random flight” treatment of molecular configuration. This power should approach 0.60 for long chain molecules in good solvents. With increase in size of the solvent molecule, the influence of

interference on molecular configuration diminishes, vanishing entirely in the extreme case of a solvent which is also a high polymer. The effect of a heat of interaction between solvent and polymer may also be incorporated quantitatively in the theory. A positive heat of mixing (poor solvent) tends to offset the expansive influence of interference, and the exponent referred to above tends to approach 0.50. The results are of foremost significance in the interpretation of the intrinsic viscosity and its dependence on the polymer constitution and on the solvent. It is pointed out that the spatial dimensions of the irregularly coiled polymer molecule cannot be correlated directly with hindrance to rotation about chain bonds, unless the expansion of the configuration due to interference and the effects of the heat of dilution are first of all taken into account.



Nobel Prize in Chemistry 1974

For predicting the "spatial configuration of macromolecular chains".



Paul Flory



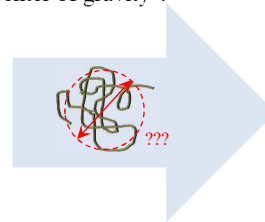
The Size of a Coil

So what is now the size of a polymer molecule?

The physical size of a coil is often described by the *radius of gyration* R_g , which is "the mean squared distance of each point on the object from its center of gravity".

For a random walk, one can relate R_g to R by:

$$R_g = R \left[\frac{1}{6} \right]^{1/2}$$



Note that R_g is indeed a radius, so the diameter is $2R_g$.

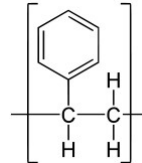
Experimental data (like light scattering) will tend to give the *hydrodynamic radius*, which is not the same thing as R_g but similar in magnitude.

Whatever parameter we use it will be proportional to the end-to-end distance, so R (or R_F) is a characteristic length that represents the size of the polymer!



Demonstration: Good Solvent

How much polystyrene can fit in a beaker?



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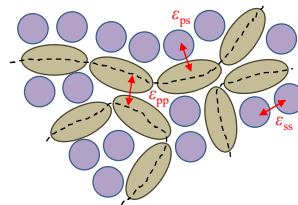
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Interactions with a Solvent

We looked at entropic effects of chain configuration and excluded volume. In a solvent we also need to consider the energy of the molecular interactions (non-covalent):

- Polymer and solvent (ϵ_{ps}).
- Polymer and polymer (ϵ_{pp}).
- Solvent and solvent (ϵ_{ss}).



Intuitively, it is clear that polymers will occupy a larger volume if they “like” the solvent. (Unless the solvent likes itself very much...)

If interactions between polymer and solvent are not favored (or if the polymer likes itself very much) we expect the polymer to occupy a smaller volume.

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The Number of Interactions

Assume there are z “contact points” between a segment of a polymer or a solvent molecule and that only nearest neighbors count (regular solution model).

We have N segments (each with volume v) within a volume r^3 . Assume the probability that a neighbor of a polymer segment is another polymer segment is equal to the volume fraction of polymer segments Nv/r^3 . We have Nz contact points to the polymer in total, so the number of polymer-polymer interactions is:

$$n_{pp} = \frac{Nz}{2} \times \frac{Nv}{r^3} = \frac{zvN^2}{2r^3}$$

We divide by two because otherwise we count the same interaction twice! The volume fraction of solvent is $1 - Nv/r^3$ so the number of polymer-solvent interactions is:

$$n_{ps} = Nz \left[1 - \frac{Nv}{r^3} \right]$$

We can write the number of solvent-solvent interactions as:

$$n_{ss} = n_0 - n_{pp} - n_{ps} = n_0 - Nz \left[1 - \frac{Nv}{r^3} \right] - \frac{zvN^2}{2r^3}$$

Here n_0 is the number of solvent-solvent interactions in the absence of the polymer.



A Single Solvent Interaction Parameter

Now we can write the total interaction energy:

$$\begin{aligned} W_{\text{int}} &= n_{pp}\varepsilon_{pp} + n_{ps}\varepsilon_{ps} + n_{ss}\varepsilon_{ss} = \\ &= \frac{zvN^2}{2r^3} \varepsilon_{pp} + zN \left[1 - \frac{vN}{r^3} \right] \varepsilon_{ps} + \left[n_0 - \frac{zvN^2}{2r^3} - zN \left[1 - \frac{vN}{r^3} \right] \right] \varepsilon_{ss} = \\ &= \frac{zvN^2}{2r^3} [\varepsilon_{pp} - 2\varepsilon_{ps} + \varepsilon_{ss}] + \underbrace{zN[\varepsilon_{ps} - \varepsilon_{ss}] + n_0\varepsilon_{ss}}_{\text{constant}} \end{aligned}$$

Just as in the excluded volume argument by Flory, the critical parameter is r . Next, we introduce the dimensionless parameter:

$$\chi = -\frac{z}{2k_B T} [\varepsilon_{pp} + \varepsilon_{ss} - 2\varepsilon_{ps}]$$

So we can write the interaction energy as:

$$W_{\text{int}} = -\frac{k_B T v \chi N^2}{r^3} + \text{constant}$$

Note that higher ε_{ps} makes χ higher and that W_{int} is proportional to r^{-3} .



The Theta Solvent

Now recall Flory's excluded volume argument and introduce the solvent interactions as another parameter in the total free energy:

$$G(r) = \frac{3k_B T r^2}{2abN} + \frac{k_B T v N^2}{r^3} + \frac{k_B T v \chi N^2}{r^3} + \text{constant}$$

conformational entropy
excluded volume
solvent interactions

We can rewrite the excluded volume and solvent interaction terms as one:

$$G(r) = \frac{3k_B T r^2}{2abN} + \frac{k_B T v N^2}{r^3} [1 - \chi] + \text{constant}$$

For $\chi = 1$ we can remove the entire second term! The result will be the random walk!
The excluded volume effect perfectly compensates the solvent interaction energies. This is known as the *theta solvent* condition.



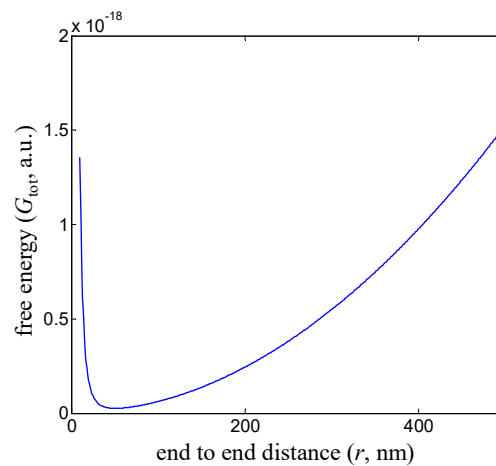
The Solvent Effect

Plot of total free energy as a function of r for:

$$\begin{aligned} T &= 300 \text{ K} \\ N &= 1000 \\ a &= b = 1 \text{ nm} \\ v &= 1 \text{ nm}^3 \\ \chi &= 1/3 \end{aligned}$$

There is still an energy minimum at roughly the same value for r !

The solvent "does not do much" for modest values of χ !





Energy Minimization in Solvent

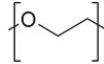
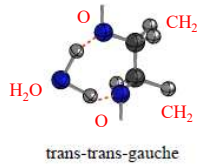
We can perform the same energy minimization calculation as for the Flory radius:

$$\frac{\partial G}{\partial r} = \frac{3k_B T r}{abN} - \frac{3k_B T v [1 - \chi] N^2}{r^4} \quad R_F = [abv[1 - \chi]]^{1/5} N^{3/5}$$

The “ordinary” Flory radius is clearly recovered for $\chi = 0$! When $\chi < 1$, we still have the same scaling relation, that is R proportional to $N^{3/5}$.

So the solvent effectively changes the excluded volume effect. We can set $\chi = 0$ as long as we keep in mind that v changes if you change solvent.

Actually, even a and b can change with solvent! For instance, hydrogen bonding locks subsequent ether oxygens in poly(ethylene glycol) at $a = 0.28$ nm.



Oosterhelt et al.
New Journal of Physics 1999, 1, 6.

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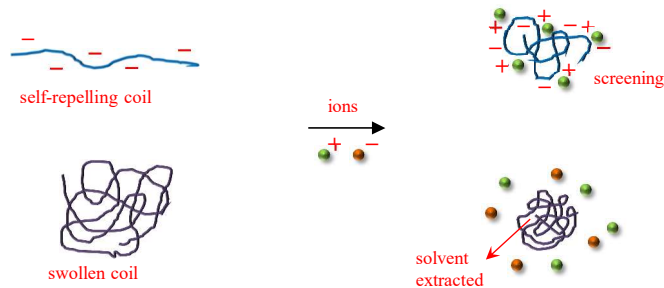
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Other Environmental Effects

The χ parameter depends on environmental factors other than just solvent type!

One example is ionic strength: Self-repulsion of charged chains can be screened by counterions and hydrophilic polymers can be shrunk by osmotic pressure.



Some polymers can undergo chemical changes with pH (protonation), thereby changing their charge, so pH is another factor that can influence χ (and maybe a or b).

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Globule States

When $\chi > 1$ we cannot calculate R_F (negative number to the power of $1/5$). The unfavorable interactions with the solvent overcome the excluded volume effect!

In essence this shows a phase transition: The polymer collapses into a compact *globule* state! The scaling relation for R is now to $N^{1/3}$.



coil ($\chi < 1$)

$$R \propto N^{3/5}$$



theta solvent ($\chi = 1$)

$$R \propto N^{1/2}$$



globule ($\chi > 1$)

$$R \propto N^{1/3}$$

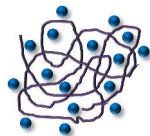
Consider the globule as spherical ball containing only polymer with volume $V = Na^3$. Since the end-to-end distance R must be proportional to the physical size we get R proportional to $N^{1/3}$.



Critical Solution Temperatures

Higher temperature generally promotes mixing due to the entropy gain, but not if the solvent loses too much entropy due to limited bond configurations (hydrophobic effect).

The same holds for polymers: Some will go from solvated to collapsed upon increased temperature. They have a *lower critical solution temperature* instead of an upper temperature above which they are always solvated.



mixed phase



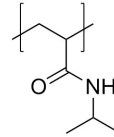
phase separated

Regardless, there will always be a *theta temperature* at which there is a transition and the solvent becomes a theta solvent.



Demonstration: Thermoresponsive Polymer

Poly(N-isopropylacrylamide) undergoes a LCST transition at $\sim 32^\circ\text{C}$ in water.



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Polymers Attached to Surfaces

Consider a planar surface onto which the polymer can be attached in some way.

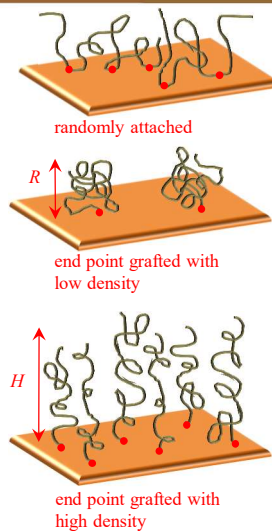
Randomly attached segments are hard to model...

Can we understand what happens when only the end point is attached? This is often the case in reality since the end group is chemically different!

Assume we have Γ polymers attached per unit area. (Same meaning of Γ as in previous lectures.)

If $\Gamma < 1/R^2$ there is no interaction and the coils extend approximately a distance of R . Not so exciting...

But what happens when the grafting density is high so the coils overlap, i.e. $\Gamma > 1/R^2$?



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Finding the Brush Height

We start with the conformational entropy. Assume that the other endpoint is located just at the average extension H . We thus replace r with h in the free energy from stretching:

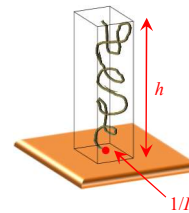
$$G_{\text{con}}(h) = \frac{3k_B T h^2}{2abN} + \text{constant}$$

Dealing with excluded volume is also quite simple. We can assume each coil occupies a volume of h/Γ (instead of r^3). The grafting density Γ is fixed. The entropy loss from self avoidance is per segment:

$$\Delta S_{\text{seg}} = k_B \log \left(\frac{\frac{h}{\Gamma} - vN}{\frac{h}{\Gamma}} \right) = k_B \log \left(1 - \frac{vN\Gamma}{h} \right) \approx -\frac{k_B vN\Gamma}{h}$$

So we get the free energy contribution as before:

$$G_{\text{vol}}(h) = \frac{k_B T v \Gamma N^2}{h}$$



The Solvent Effect for Brushes

Now recall the total interaction energy for solvent effects. Again, the only difference is that the volume is now h/Γ instead of r^3 :

$$W_{\text{int}} = \frac{zv\Gamma N^2}{2h} [\epsilon_{\text{pp}} - 2\epsilon_{\text{ps}} + \epsilon_{\text{ss}}] + \underbrace{zN[\epsilon_{\text{ps}} - \epsilon_{\text{ss}}] + n_0\epsilon_{\text{ss}}}_{\text{constant with respect to } h}$$

We can define χ just like before and write the interaction energy as:

$$W_{\text{int}} = -\frac{k_B T v \chi \Gamma N^2}{h} + \text{constant}$$

So we now have all three free energy terms for the brush:

$$G(h) = \frac{3k_B T h^2}{2abN} + \frac{k_B T v \Gamma N^2}{h} [1 - \chi] + \text{constant}$$

You should know what to do next...



The Alexander - de Gennes Brush

As before, we find the end-to-end distance that minimizes the free energy (now H):

$$\frac{\partial G}{\partial h} = \frac{3k_B T h}{abN} - \frac{k_B T v \Gamma N^2}{h^2} [1 - \chi]$$

If we ignore the solvent parameter ($\chi = 0$) we get the solution:

$$H = \left[\frac{abv\Gamma}{3} \right]^{1/3} N$$

We see that H scales linearly with N (not like coils in solution).

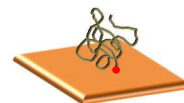
Also, we see that H is proportional to $\Gamma^{1/3}$, so brush height depends very weakly on grafting density (a bit counterintuitive).



Sanity Check: Extreme Grafting Densities

Let us see what happens when the coils are barely overlapping: $\Gamma = R_F^{-2}$

$$H = \left[\frac{abv}{3[abv]^{1/5} N^{3/5}} \right]^{1/3} N = \left[\frac{1}{3} \right]^{1/3} [abv]^{1/5} N^{3/5} = \left[\frac{1}{3} \right]^{1/3} R_F$$



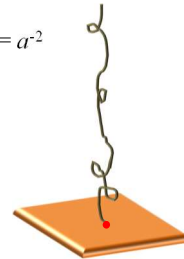
$$H \approx R_F$$

Almost $H = R_F$ which makes sense, but different scaling with N .

Highest possible grafting density must correspond to monomer area: $\Gamma = a^{-2}$

$$H = \left[\frac{abv}{3a^2} \right]^{1/3} N = \left[\frac{1}{3} \right]^{1/3} \left[\frac{bv}{a} \right]^{1/3} N$$

As long as b is comparable to a and v comparable to a^3 we get H comparable to aN (contour length) so everything seems fine.



$$H \approx aN$$



Brush Density

We can calculate the volume fraction Φ inside the brush.

The volume of one strand is Na^3 .

The volume occupied of one coil is H/Γ so:

$$\Phi = \frac{\Gamma Na^3}{H} = \frac{\Gamma Na^3}{\left[\frac{abv\Gamma}{3}\right]^{1/3} N} = \frac{a^{8/3} \Gamma^{2/3}}{\left[\frac{bv}{3}\right]^{1/3}}$$

Depends on grafting density but not N !

Completely different compared to the monomer density inside a coil in solution!

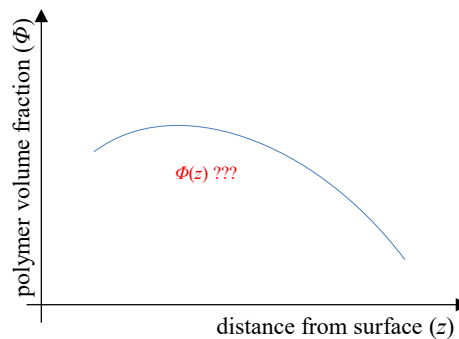


Model Limits

The Alexander - de Gennes brush is *strongly stretched*. We assume the opposite end of the polymer is at the “top” of the brush! This leads to some problems:

- Scaling relation as proportional to N is only valid if Γ is high.
- Monomer *density profile* is constant and not very accurate.

$$\int_0^\infty \frac{\Phi}{a^3} dz = \Gamma N$$





Monomer Density Profiles

The de Gennes “step function” height multiplied by 1.3 gives the end point of the more accurate parabolic profile (derived by Milner).

Strictly speaking the brush height is not so easy to define...

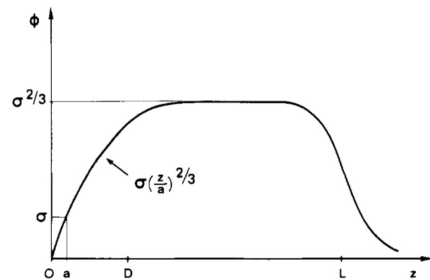


Figure 6. Concentration profile for a grafted layer immersed in a good solvent in the overlapping regime.

de Gennes
Macromolecules **1980**, 13 (5), 1069-1075.

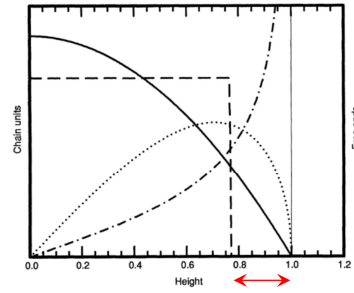


Fig. 2. Chain-unit density profiles $\phi(z)$ for a “parabolic” brush (that is, $\phi \ll 1$ so $\mu \approx \phi$), and the step-function ansatz at equal coverage σ and chain length N . Also shown are end-density profiles for brushes with (dotted) and without (dot-dashed) solvent.

Milner
Science **1991**, 251 (4996), 905-914.

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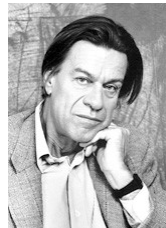
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Nobel Prize in Physics 1991

A guru in soft matter in general, especially known for his work with liquid crystals and polymer brushes.



Pierre-Gilles de Gennes

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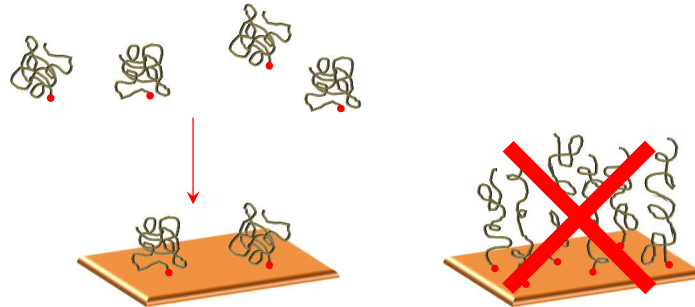
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Preparation of Polymer Brushes

The chemistry is often straightforward: For instance, a thiol (-SH) terminal group can be grafted to gold or triethoxysilanes (-Si(OCH₂CH₃)₃) to silica.

However, if the coils do not overlap spontaneously in solution, why would they do that on a surface? How can we get $\Gamma > 1/R^2$?



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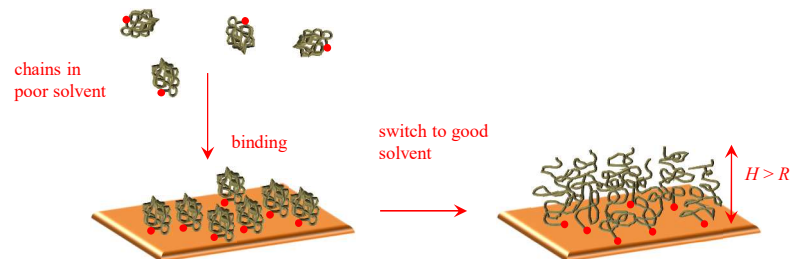
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Grafting to the Surface

The grafting density is increased if the polymer is smaller when binding to the surface. Under theta solvent conditions the polymers in solution are smaller ($R \sim N^{1/2}$). When switching to a good solvent, the polymer extends ($R \sim N^{3/5}$).

However, this “cloud point” grafting does not always result in really high Γ .



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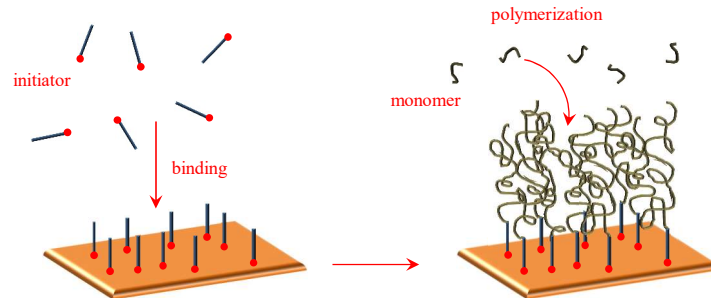
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Surface Initiated Polymerization

The polymerization reaction is performed at the surface.

A small initiator is first bound to the surface in a dense monolayer. As a result, Γ can be high. This is referred to as "grafting from" methods.



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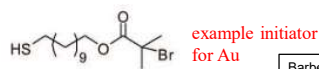
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Atom Transfer Radical Polymerization

Most common method in grafting-from is *atom transfer radical polymerization* (ATRP).

- *Activator* steals group (usually -Br) from *initiator* to generate radical.
- Monomer should preferably have acrylate or methacrylate group.
- Requires O_2 free environments since radicals react with it.
- ATRP can be more or less "living" depending on rate of termination events.



Barbey et al.
Chemical Reviews 2009, 109 (11), 5437-5527.

Polymer	Chemical structure
METHACRYLATES (Neutral)	
PAHMA poly(6-azidoheptyl methacrylate)	
PBIEMA poly(2-(2-bromoisobutyloxy)ethyl methacrylate)	
PBMA poly(n-butyl methacrylate)	
PBzMA poly(benzyl methacrylate)	
ACRYLATES (Neutral)	
PAA poly(acrylic acid) (sodium salt form, of PAA(Na))	
PAAB poly(acrylated antibody)	
PBA poly(n-butyl acrylate)	
PBAEA poly(2-(bromoisobutyloxy)ethyl acrylate)	

monomer examples

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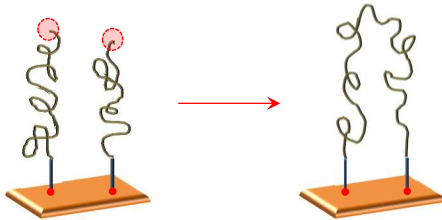


Termination

Loops may be formed if chains close to each other are in the active state at the same time (radical combination).

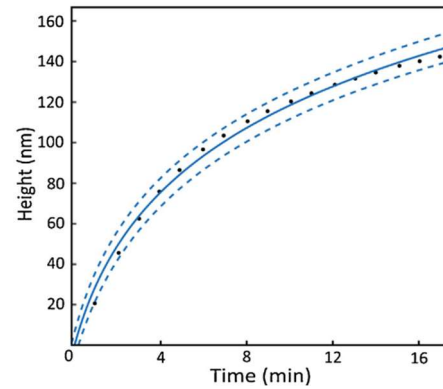
This can make the brush growth non-linear and limit how thick it can become!

Too fast growth (many active chains) is usually more problematic.



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Emilsson et al.
Applied Surface Science 2017, 396, 384-392.

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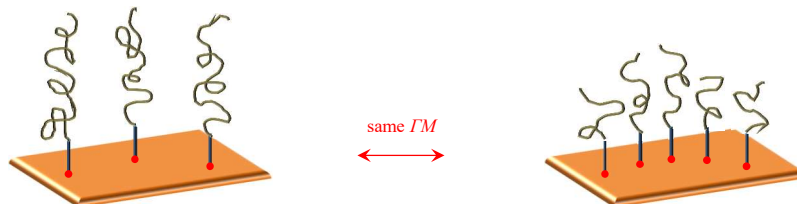
Getting the Grafting Density

Using surface sensitive techniques (e.g. SPR), we can at best only determine the mass coverage ΓM (e.g. ng/cm²). We cannot get individual values for surface coverage (number of molecules per area) or molecular weight.

Techniques used to determine polymer M (mainly chromatography) cannot be used when the molecules are attached to a surface.

Even if we manage to remove the polymers and collect them, the amount of material is normally not enough for analysis.

Here grafting has a clear advantage because you can characterize the polymer beforehand, so M is known. Then Γ can be calculated based on experimental data.



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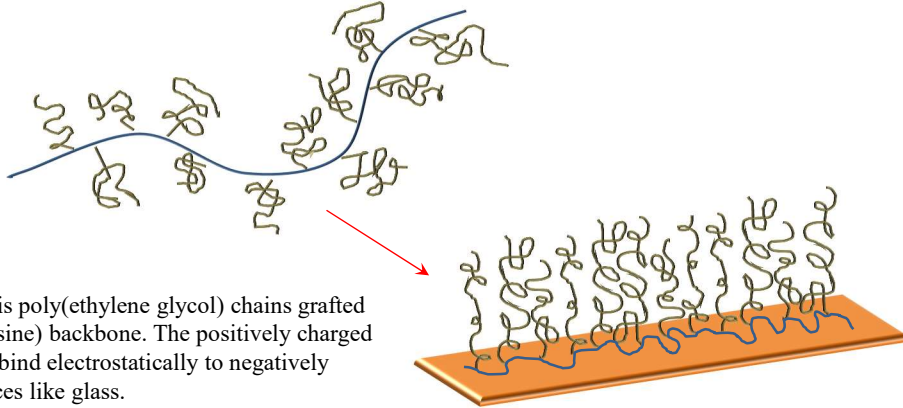
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Branched Block Copolymers

Another way to generate a brush is to have the polymer of interest as blocks attached to a backbone which binds to the surface (similar to grafting-to). Also known as “bottlebrush” polymers.



One example is poly(ethylene glycol) chains grafted to a poly(L-lysine) backbone. The positively charged lysine groups bind electrostatically to negatively charged surfaces like glass.

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Checklist 5

- The entropic spring model
- Excluded volume entropy (osmotic pressure)
- Solvent interactions
- Scaling laws for Flory radius and de Gennes brush (N and I)
- LCST behavior and collapsed chains
- Monomer density (average values and profiles)
- How to make brushes, “grafting to” vs “grafting from”

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Exercise 5.1

A polymer has monomer length 0.5 nm, Kuhn length 1 nm and excluded volume 0.1 nm^3 in a good solvent. Estimate the polymer volume fraction inside a coil in solution for $N = 100$ and $N = 1000$. (You need to somehow express the volume of monomers and estimate the total volume that the coil occupies.)



Exercise 5.1

The volume fraction of polymer inside its own coil is approximately:

$$\phi = \frac{Na^3}{R_F^3} = \frac{Na^3}{[[abv]^{1/5}N^{3/5}]^3} = a^{12/5}[bv]^{-3/5}N^{-4/5}$$

Note that we use a^3 for the physical size of the monomer, but not for the excluded volume parameter since that contains solvent effects. This is the most accurate way with the information available!

The answers for the different N :

$$\phi = 0.5^{12/5}[1 \times 0.1]^{-3/5}100^{-4/5} = 0.018 \dots$$

$$\phi = 0.5^{12/5}[1 \times 0.1]^{-3/5}1000^{-4/5} = 0.0030 \dots$$

Important to note that the "density" of the coil decreases with N .

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Exercise 5.2

For a strongly stretched brush of poly(N-isopropylacrylamide) with $M = 50$ kg/mol, each coil occupies 500 \AA^2 on the surface. The monomer has length $a = 3.0 \text{ \AA}$ (and can be written as $\text{C}_6\text{H}_{10}\text{ON}$). The Kuhn length is 5 nm and you may assume $\nu = a^3$. What is the thickness of the brush?

→

62 nm

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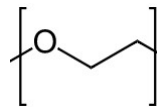
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Exercise 5.3

A brush of poly(ethylene glycol) with 20 kg/mol is 50 nm thick. The grafting density is 0.28 nm^{-2} . The monomer has length $a = 0.28 \text{ nm}$ and the Kuhn length is 0.72 nm . What is the excluded volume parameter (ν)? (Compare with a^3 .)

→

0.07 nm³

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Exercise 5.4

A polymer brush has a thickness which is 80% of its maximum value. The grafting density is 0.5 nm^{-2} and the monomer length is 0.5 nm . You may assume that the excluded volume parameter is the cube of the monomer length. What is then the Kuhn length?

→

6.14 nm

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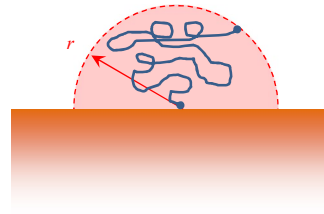
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Exercise 5.5

One often says that when $\Gamma < R_F^{-2}$ end point grafted polymers extend approximately a distance of R_F . Calculate the extension r from the surface under the assumption that the coil occupies a half-spherical volume and the free end is always on the surface on this sphere (express the answer in terms of R_F).

→

$$[3/[2\pi]]^{1/5} R_F$$


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